hindrance.

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agents.

1	1. Functionalized metal oxide particles comprising?
2	a surface comprising a total quantity of hydroxyl groups comprising a complexed
3	fraction comprising a reactive portion and a less reactive portion;
4	said reactive portion being complexed with functionalities selected from the group
5	consisting of functionalities with high steric hindrance, functionalities with
6	low steric hindrance, and a combination thereof;

2. The functionalized metal oxide particles of claim 1 wherein said functionalities having a low/steric hindrance comprise mobile adhesion promoters and said functionalities having a high steric hindrance comprise organofunctional coupling

said less reactive portion being complexed with said groups having a low steric

- 1 3. The functionalized metal oxide particles of claim 1 wherein said 2 complexed fraction is effective to produce a coagulation point of about 1 minute or more.
- 1 4. The functionalized metal oxide particles of claim 1 wherein said 2 complexed fraction is effective to produce a coagulation point of about 1 hour or more.
- 1 5. The functionalized metal oxide particles of claim 2 wherein said 2 complexed fraction is effective to produce a coagulation point of about 1 minute or more.

1	6.	The	functionalized	metal	oxide	particles	of	claim	2	wherein	.8aid
2	complexed fra	ection	is effective to pr	roduce a	a coagu	lation poir	ıt of	about 1	ho	our or mor	e.
					/.						
1	7.	The	functionalized	metal	oxide	particles	of	claim	1	wherein	said
2	complexed fra	ection	is about 50% or	more o	f said to	otal quanti	ty.				
1	8.	The	functionalized	metal	oxide	particles	of	claim	2	wherein	said
2	organofunctio	nal co	oupling agents a	are irrev	versibly	conplexe	d) wi	th said	re	active poi	tion.
		/		/							
1	9.	The	functionalized	metal	oxide	particles	of	claim	1	wherein	said
2	complexed fra	ction	comprises subst	antially	all of s	aid total q	uant	ity.			
人											
HER	10/	The	functionalized	metal	oxide	particles	of	claim	2	wherein	said
3	complexed fra	action	comprises subst	antially	all of s	aid total q	uant	ity.			
						·					
1	1.	The	functionalized	metal	oxide	particles	of	claim	3	wherein	said
2	complexed fra	action	comprises subst	antially	all of s	aid total q	uant	ity.			
		/									
1	2.	The	functionalized	metal	oxide	particles	of	claim	4	wherein	said
2	complexed fra	action	comprises subst	antially	all of s	aid total q	uant	ity.			

The functionalized metal oxide particles of claim 5 wherein said

complexed fraction comprises substantially all of said total quantity.

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- 1 14. The functionalized metal oxide particles of claim 6 wherein said 2 complexed fraction comprises substantially all of said total quantity.
 - 15. Functionalized metal oxide particles comprising a surface comprising a total quantity of bydroxyl groups comprising a complexed fraction and an uncomplexed fraction, said complexed fraction being effective to produce a coagulation point of about one minute or more after removal of a solvent from a mixture of said metal oxide particles and a matrix resin.
 - 16. The functionalized metal oxide particles of claim 15 wherein said complexed fraction is effective to produce a coagulation point of about one hour or more after removal of a solvent.
 - The functionalized metal oxide particles of claim 15 wherein said complexed portion comprises a less reactive portion complexed with a mobile adhesion promoter and a more reactive portion complexed with an organofunctional coupling agent.
 - 78. The functionalized metal oxide particles of claim 16 wherein said complexed portion comprises a less reactive portion complexed with a mobile adhesion promoter and a more reactive portion complexed with an organofunctional coupling agent.

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1	19.	The	functionalized	metal	oxide	particles	of	claim	17	wherein the
2	organofunctio	mal co	- oupling agent als	o comp	rises an	adhesion	pror	noter.		

20. The functionalized metal oxide particles of claim 18 wherein the rganofunctional coupling agent also comprises an adhesion promoter.

- The functionalized metal oxide particles of claim 1 wherein the metal oxide comprises a metal selected from the group consisting of niobium, indium, titanium, zinc, zirconium, tin, cerium, hafnium, tantalum, tungsten, bismuth, silicon and combinations thereof.
 - 22. The functionalized metal oxide particles of claim wherein said metal oxide comprises a metal selected from the group consisting of niobium, indium, titanium, zinc, zirconium, tin, cerium, hafnium, tantalum, tangsten, bismuth, and combinations thereof.
- The functionalized metal oxide particles of claim 3 wherein the metal oxide comprises a metal selected from the group consisting of niobium, indium, titanium, zinc, zirconium, tin, cerium, hafnium, tantalum, tungsten, bismuth, silicon and combinations thereof.
- The functionalized metal oxide particles of claim 4 wherein said metal oxide comprises a metal selected from the group consisting of niobium, indium, titanium,

The functionalized metal oxide particles of claim 21 wherein said metal oxide comprises a metal selected from the group consisting of niobium, indium. titanium.

zinc, zirconium, tin, cerium, hafnium, tantalum, tungsten, bismuth, and combinations

4 thereof.

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The functionalized metal oxide particles of claim 22 wherein said metal oxide comprises a metal selected from the group consisting of niobium, indium, titanium, zinc, zirconium, tin, cerium, hafnium, tantalum, tungsten, bismuth, and combinations thereof.

The functionalized metal oxide particles of claim 23 further comprising an alloying element selected from the group consisting of aluminum, phosphorus, gallium, germanium, barium, strontium, yttrium, niobium, antimony, cesium, and combinations thereof

4 thereof.

28. The functionalized metal oxide particles of claim 24 further comprising an alloying element selected from the group consisting of aluminum, phosphorus, gallium, germanium, barium, strontium, yttrium, niobium, antimony, cesium, and combinations thereof.

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1	29. The functionalized metal oxide particles of claim 25 further comprising an
2	alloying element selected from the group consisting of aluminum, phosphorus, gallium,
3	germanium, barium, strontium, yttrium, niobium, antimony, cesium, and combinations
4	thereof.
/	
1/	30. The functionalized metal oxide particles of claim 26 further comprising an
2	alloying element selected from the group consisting of aluminum, phosphorus, gallium,
χ_3	germanium, barium, strontium, yttrium, niobium, antimony, cesium, and combinations
(4)	thereof.

- 31. The functionalized metal oxide particles of claim 27 further comprising an alloying element selected from the group consisting of aluminum, phosphorus, gallium, germanium, barium, strontium, yttrium, niobium, antimony, cesium, and combinations thereof.
- 32. The functionalized metal oxide particles of claim 28 further comprising an alloying element selected from the group consisting of aluminum, phosphorus, gallium, germanium, barium, strontium, yttrium, niobium, antimony, cesium, and combinations thereof:
- 1 33. The functionalized metal oxide particles of claim 1 wherein said metal 2 comprises zirconium.

1	34.	The functionalized metal oxide particles of claim 2 wherein said metal
2	comprises zirce	onium.
1	35.	The functionalized metal oxide particles of claim 3 wherein said metal
2	comprises zirc	onium.
1	36.	The functionalized metal oxide particles of claim 4 wherein said metal
2	comprises zirco	onium.
1	37.	The functionalized metal oxide particles of claim 17 wherein said metal
2	comprises zirco	onium.
÷	Λ	
1	38	The functionalized metal oxide particles of claim 18 wherein said metal
2	comprises zirce	onium.

1 39. The functionalized metal oxide particles of claim 1 further comprising a mixture comprising a matrix resin comprising monomers comprising functional groups polymerizable with said organofunctional coupling agents.

40. The functionalized metal oxide particles of claim 2 further comprising a mixture comprising a matrix resin comprising monomers comprising functional groups polymerizable with said organofunctional coupling agents.

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- 1 41. The functionalized metal oxide particles of claim 5 further comprising a mixture comprising a matrix resin comprising monomers comprising functional groups polymerizable with said organofunctional coupling agents.
- 1 42. The functionalized metal oxide particles of claim 6 further comprising a 2 mixture comprising a matrix resin comprising monomers comprising functional groups 3 polymerizable with said organofunctional coupling agents.
 - 43. The functionalized metal oxide particles of claim 17 further comprising a mixture comprising a matrix resin comprising monomers comprising functional groups polymerizable with said organofunctional coupling agents.
 - 44. The functionalized metal oxide particles of claim 18 further comprising a mixture comprising a matrix resin comprising monomers comprising functional groups polymerizable with said organofunctional coupling agents.
 - 45. The functionalized metal oxide particles of claim 1 comprising an average diameter effective to permit curing of said mixture by photopolymerization.
- 1 46. The functionalized metal oxide particles of claim 2 comprising an average 2 diameter effective to permit curing of said mixture by <u>photopolymerization</u>.
- 1 47. The functionalized metal oxide particles of claim 5 comprising an average 2 diameter effective to permit curing of said mixture by photopolymerization.

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- 1 48. The functionalized metal oxide particles of claim 6 comprising an average 2 diameter effective to permit curing of said mixture by photopolymerization.
 - 49. The functionalized metal oxide particles of claim 17 comprising an average diameter effective to permit curing of said mixture by photopolymerization.
 - 50. The functionalized metal oxide particles of claim 18 comprising an average diameter effective to permit curing of said mixture by photopolymerization.
 - 51. The functionalized metal oxide particles of claim 2 wherein a sufficient quantity of said reactive portion is complexed with an organofunctional coupling agent to provide fracture toughness of a cured composite comprising said functionalized metal oxide particles.
 - 52. The functionalized metal oxide particles of claim 5 wherein said a sufficient quantity of said reactive portion is complexed with said organofunctional agent to provide fracture toughness of a cured composite comprising said functionalized metal oxide particles.
 - 53. The functionalized metal oxide particles of claim 6 wherein said a sufficient quantity of said reactive portion is complexed with said organofunctional agent to provide fracture toughness of a cured composite comprising said functionalized metal oxide particles.

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- The functionalized metal oxide particles of claim 17 wherein said a sufficient quantity of said reactive portion is complexed with said organofunctional agent to provide fracture toughness of a cured composite comprising said functionalized metal oxide particles.
 - 55. The functionalized metal exide particles of claim 18 wherein said a sufficient quantity of said reactive portion is complexed with said organofunctional agent to provide fracture toughness of a cured composite comprising said functionalized metal oxide particles.
 - 56. The functionalized metal oxide particles of claim 2 wherein the organofunctional coupling agent comprises a polymerizable group selected from the group consisting of one or more vinyl groups, acryl groups, epoxy groups, or methacryl groups.
 - 57/ The functionalized metal oxide particles of claim 5 wherein the organofunctional coupling agent comprises a polymerizable group selected from the group consisting of one or more vinyl groups, acryl groups, epoxy groups, or methacryl groups.
- The functionalized metal oxide particles of claim 6 wherein the organofunctional coupling agent comprises a polymerizable group selected from the

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- group consisting of one or more vinyl groups, acryl groups, epoxy groups, or methacrylgroups.
- The functionalized metal oxide particles of claim 17 wherein the organofunctional coupling agent comprises a polymerizable group selected from the group consisting of one or more vinyl groups, acryl groups, epoxy groups, or methacryl groups.
 - The functionalized metal oxide particles of claim 18 wherein the organofunctional coupling agent comprises a polymerizable group selected from the group consisting of one or more vinyl groups, acryl groups, epoxy groups, or methacryl groups.
 - organofunctional coupling agent comprises a functionality selected from the group consisting of mono-, di-, and tri-functional silanes, isocyanates, zirconates, aluminozirconates, zirconyl methacrylate, titanates, and phosphonates.
 - organofunctional coupling agent comprises a functionality selected from the group consisting of mono-, di-, and tri-functional silanes, isocyanates, zirconates, aluminozirconates, zirconyl methacrylate, titanates, and phosphonates.

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1	63. The functionalized metal oxide particles of claim 58 wherein the
2	organofunctional coupling agent comprises a functionality selected from the group
3	consisting of mono-, di-, and tri-functional silanes, isocyanates, zirconates,
4	aluminozirconates, zirconyl methacrylate, titanates, and phosphorates.

- 64. The functionalized metal oxide particles of claim 59 wherein the organofunctional coupling agent comprises a functionality selected from the group consisting of mono-, di-, and tri-functional silanes, isocyanates, zirconates, aluminozirconates, zirconyl methacry late, titanates, and phosphonates.
- 65. The functionalized metal oxide particles of claim 60 wherein the organofunctional coupling agent comprises a functionality selected from the group consisting of mono-, di-, and tri-functional silanes, isocyanates, zirconates, aluminozirconates, zirconyl methacrylate, titanates, and phosphonates.
- 66. The functionalized metal oxide particles of claim 2 wherein the organofunctional groups are hydrolyzable zirconates having the following general structure:

$$R^1$$
 -O- Zr - $(OR^2)_3$

5 wherein

- R¹ is selected from the group consisting of hydrolyzable alkyl groups and hydrolyzable alkenyl groups having 1 or more carbon atoms; and
- R² is selected from the group consisting of copolymerizable alkenyl substituents containing 2 or more carbon atoms.

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1	67. The	e functional	ized metal	oxide partic	cles of claim	n 5 whereir	1 the
2	organofunctional	groups are	hydrolyzable	e zirconates	having the	following ge	eneral
3	structure:						

$$R^{1}$$
-O- Zr-(OR²)₃

5 wherein

R¹ is selected from the group consisting of hydrolyzable alkyl groups and hydrolyzable alkenyl groups having 1 or more carbon atoms; and

R² is selected from the group consisting of copolymerizable alkenyl substituents containing 2 or more carbon atoms.

68. The functionalized metal oxide particles of claim 6 wherein the organofunctional groups are hydrolyzable zirconates having the following general structure:

$$R^1$$
 -O- Zr - $(OR^2)_3$

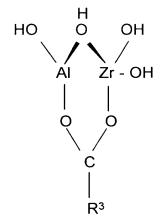
wherein

R¹ is selected from the group consisting of hydrolyzable alkyl groups and hydrolyzable alkenyl groups having 1 or more carbon atoms; and

R² is selected from the group consisting of copolymerizable alkenyl substituents containing 2 or more carbon atoms.

69. The functionalized metal oxide particles of claim 17 wherein the organofunctional groups are hydrolyzable zirconates having the following general structure:

- The functionalized metal oxide particles of claim 68 wherein R¹ is selected from the group consisting of alkyl groups having from about 1 to about 9 carbon atoms.
- The functionalized metal oxide particles of claim 69 wherein R¹ is selected from the group consisting of alkyl groups having from about 1 to about 9 carbon atoms.
 - 75. The functionalized metal oxide particles of claim 70 wherein R¹ is selected from the group consisting of alkyl groups having from about 1 to about 9 carbon atoms.
 - 76. The functionalized metal oxide particles of claim 2 wherein the organofunctional groups comprise moeities selected from the group consisting of neopentyl (diallyl) oxy trimethacryl zirconates, neopentyl (diallyl) oxy triacryl zirconates, and aluminozirconates having the following general structure:



wherein R³ is selected from the group consisting of copolymerizable alkenyl groups and carboxyfunctional substituents containing 1 or more carbon atoms.

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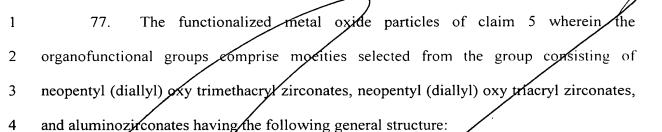
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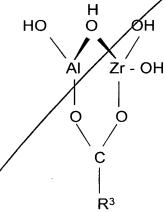
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wherein R³ is selected from the group consisting of copolymerizable alkenyl groups and carboxyfunctional substituents containing 1 or more carbon atoms.

78. The functionalized metal oxide particles of claims 6 wherein the organofunctional groups comprise moeities selected from the group consisting of neopental (diallyl) oxy trimethacryl zirconates, neopental (diallyl) oxy triacryl zirconates,

4 and aluminozirconates having the following general structure:

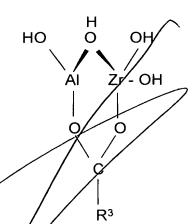
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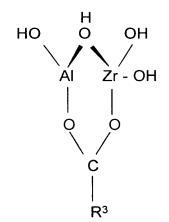
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wherein R³ is selected from the group consisting of copolymerizable alkenyl groups and carboxyfunctional substituents containing 1 or more carbon atoms.

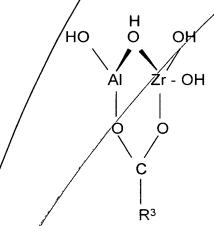
79. The functionalized metal oxide particles of claim 17 wherein the organofunctional groups comprise moeities selected from the group consisting of neopentyl (diallyl) oxy trimethacryl zirconates, neopentyl (diallyl) oxy triacryl zirconates, and aluminozirconates having the following general structure:



wherein R is selected from the group consisting of copolymerizable alkenyl

6 groups and carboxyfunctional substituents containing 1 or more carbon atoms.

1 80. The functionalized metal oxide particles of claim 18 wherein the 2 organofunctional groups comprise moeities selected from the group consisting of 3 neopentyl (diallyl) oxy trimethacryl zirconates, neopentyl (diallyl) oxy triacryl zirconates, 4 and aluminozirconates having the following general structure:



wherein R³ is selected from the group consisting of copolymerizable alkenyl groups and carboxyfunctional substituents containing 1 or more carbon atoms.

- 1 81. The functionalized metal oxide particles of claim 2 wherein said 2 organofunctional groups are methacryloxy aluminozirconates.
- 1 82. The functionalized metal oxide particles of claim 5 wherein said 2 organofunctional groups are methacryloxy aluminozirconates.
- The functionalized metal oxide particles of claim 6 wherein said organoffunctional groups are methacryloxy aluminozirconates.

ester linkage to a phosphonate group.

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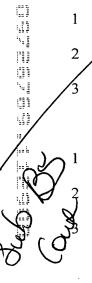
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1	88	The method	of claim	5 wherein	one or more	of Said orga	anofunctional
2	coupling age	nts and said mo	obile adhes	sion promo	ter is bound t	o the oxide s	urface via an
3	ester linkage	to a phosphona	te group.				

- 89. The method of claim 6 wherein one or more of said organofunctional coupling agents and said less reactive functionalities is bound to the oxide surface via an ester linkage to a phosphonate group.
- 90. The method of claim 17 wherein one or more of said organofunctional coupling agents and said less reactive functionalities is bound to the oxide surface via an ester linkage to a phosphonate group.
- 91. The method of claim 18 wherein one or more of said organofunctional coupling agents and said less reactive functionalities is bound to the oxide surface via an ester linkage to a phosphonate group.
- 92. The functionalized metal oxide particles of claim 86 wherein said phosphonate group comprises a silyl ester which may or may not comprise a polymerizable group.
- 93. The functionalized metal oxide particles of claim 87 wherein said phosphonate group comprises a silyl ester which may or may not comprise a polymerizable group.



94.	The	functionalize	ed	metal	oxide	partic	eles o	of c	laim	88	wherein	said
phosphonate	group	comprises	a	silyl	ester	which	may	or	may	not	compri	se a
polymerizable	e group).						7				

- 95. The functionalized metal oxide particles of claim 89 wherein said phosphonate group comprises a silyl ester which may or may not comprise a polymerizable group.
- 96. The functionalized metal oxide particles of claim 90 wherein the phosphonate group comprises a silyl ester which may or may not comprise a polymerizable group.
- 97. The functionalized metal oxide particles of claim 91 wherein the phosphonate group comprises a silyl ester which may or may not comprise a polymerizable group.
- 98. The functionalized metal oxide particles of claim 1 wherein the functionality with low steric hindrance is selected from the group consisting of silanes, phosphonates phosphates, chelating agents, fatty acids, fatty alcohols, and ester linked fatty acids.
- The functionalized metal oxide particles of claim 2 wherein the mobile adhesion promoter is selected from the group consisting of silanes, phosphonates, phosphates, chelating agents, fatty acids, fatty alcohols, and ester linked fatty acids.

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- The functionalized metal oxide particles of plaim 5 wherein the mobile 1 100. 2 adhesion promoter is selected from the group consisting of silanes, phosphonates, phosphates, chelating agents, fatty acids, fatty alcohols, and ester linked fatty acids. 3
- The functionalized metal oxide particles of claim 6 wherein the mobile 1 101. adhesion promoter is selected from the group consisting of silanes, phosphonates, 2 3 phosphates, chelating agents, fatty acids, fatty alcohols, and ester linked fatty acids.
 - 102. The functionalized metal oxide particles of claim 17 wherein the mobile adhesion promoter is selected from the group consisting of silanes, phosphonates, phosphates, chelating agents, fatty acids, fatty alcohols, and ester linked fatty acids.
 - The functionalized metal oxide particles of claim 18 wherein the mobile adhesion promoter is selected from the group consisting of silanes, phosphonates, phosphates, chelating agents, fatty acids, fatty alcohols, and ester linked fatty acids.
- The metal oxide particles of claim 2 wherein the mobile adhesion 2 promoter comprises dimethyl ethoxy vinyl silane.
- 1 105. The metal oxide particles of claim 5 wherein the mobile adhesion 2 promoter comprises dimethyl ethoxy vinyl silane.

1	106. The metal oxide particles of claim 6 wherein the mobile adhesion
2	promoter comprises dimethyl ethoxy vinyl silane.
1	107. The metal oxide particles of claim 17 wherein the mobile adhesion
2	promoter comprises dimethyl ethoxy vinyl silane.
1	108. The metal oxide particles of claim 18 wherein the mobile adhesion
2	promoter comprises dimethyl ethoxy vinyl silane.
/	
/1	109. The metal oxide particles of claim 1 having an average diameter of from
2	about 10 to about 150 nanometers.
1	110. The metal oxide particles of claim 2 having an average diameter of from
I^2	about 10 to about 150 nanometers.
1	111. The metal oxide particles of claim 3 having an average diameter of from
2	about 10 to about 150 nanometers.
1	12. The metal oxide particles of claim 4 having an average diameter of from
2	about $\int_0^1 0$ to about 150 nanometers.
1	113. A composition comprising the metal oxide particles of claim 2 and a
2	matrix comprising at least one monomer comprising a group polymerizable with the
3	organofunctional coupling agent.
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- 1 114. A composition comprising the metal oxide particles of claim 5 and a 2 matrix comprising at least one monomer comprising a group polymerizable with the 3 organofunctional coupling agent.
 - 115. A composition comprising the metal oxide particles of claim 6 and a matrix comprising at least one monomer comprising a group polymerizable with the organofunctional coupling agent.
 - 116. A composition comprising the metal oxide particles of claim 18 and a matrix comprising at least one monomer comprising a group polymerizable with the organofunctional coupling agent.
 - 117. A composite comprising the composition of claim 113 wherein said group and said organofunctional coupling agent are copolymerized.
- 1 118. A composite comprising the composition of claim 114 wherein said group
 2 and said organofunctional coupling agent are copolymerized.
- 1 119. A composite comprising the composition of claim 115 wherein said group
 2 and said organofunctional coupling agent are copolymerized.
- 1 120 A composite comprising the composition of claim 116 wherein said group 2 and said organofunctional coupling agent are copolymerized.



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121. The composition of claim 113 comprising a dental restorative composition.

122. The composition of claim 117 comprising a dental restorative composition.

123. The composition of claim 113 comprising a prototyping composition.

U 124. The composition of claim 117 comprising a prototyping composition.

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25.) A method comprising

providing metal oxide particles comprising a surface comprising a total quantity of hydroxyl groups comprising a reactive portion and a less reactive portion:

complexing said reactive portion with a functionality selected from the group consisting mobile adhesion promoters, organofunctional coupling agents,

and a combination thereof; and,

complexing said less reactive portion with said mobile adhesion promoters.

126. The method of claim 125 further comprising mixing said functionalized

metal oxide particles in a solvent with a hydrophobic matrix comprising at least one

monomer comprising a component polymerizable with the organofunctional coupling

4 agent.

- 1 127. The method of claim 125 further comprising removing said solvent from
- 2 said mixture, producing a composite that maintains a mobile state for a period longer than
- 3 the same composite in the absence of said complexed fraction.